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(54) DEVICE FOR PROTECTING PASSENGERS OF HIGH SPEED VEHICLES

(71) We, ASAHI KASEI KOGYO KABUSHIKI KAISHA, of No. 25-1, 1-chome, Dojimahamadori, Kitaku, Osaka, Japan, a body corporate of Japan. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a vehicle safety device in which a gas-generating composition rapidly inflates a human body protecting bag.

Recently because of an ever increasing number of traffic accidents, rapidly-inflatable bags used as a safety device for protecting passengers at the time of head-on or rear-end collisions of cars, have been developed. Such bags are intended to be inflated from a folded state to receive a human body moving by inertia at the time of car collision and to protect against the so-called secondary collision, which is the crash of the human body against interior portions of a car. In this case, a liquefied gas such as a fluorocarbon or carbon dioxide, or a compressed gas such as nitrogen or air, is used as a gas source for inflating the bag. The liquefied gas or compressed gas is stored in a high pressure bomb used as a gas-generating apparatus and at the time of need, a sealing plate of the bomb is broken and the gas is introduced into the interior of the bag to inflate it.

However, at present such gas-generating apparatus is not in practical use because of the following drawbacks: When the gas-generating apparatus is used to fill a bag, the sound pressure level is so high during inflation that passenger's ears are often injured. Because the volume of gas in the bag changes according to temperature, the internal pressure of the bag changes and, as a result, the performance of bags in protecting passengers fluctuates because of the influence of environmental temperature. Also there is a problem of stability of the high pressure gas-generating apparatus during storage and a large space requirement for a large-scale gas-generating apparatus when carried by a car.

On the other hand, the use of explosives or combustible compositions has been attempted. However, when such compositions are used in a safety device it is necessary that they inflate the device safely, rapidly and without forming high ignition sound pressure level. In this regard, none of the known compositions are entirely satisfactory.

According to the present invention there is provided a vehicle safety device comprising an inflatable bag, a gas generating composition positioned within the bag or in a space communicating with the bag, and means for initiating gas-generation, the gas-generating composition comprising:

(A) 10% to 80% by weight of a combustible constituent comprising:
  (1) at least one reducing agent; and
  (2) at least one inorganic oxidizing agent; and

(B) 20% to 90% by weight of a gas-generating agent comprising one or more of smokeless powder, nitrocellulose, combustible high molecular weight organic polymeric material and organic compounds easily decomposable by heat.

By using the above described gas-generating composition it is possible to inflate a body protecting bag rapidly and sufficiently with a highest degree of safety and such a low level of sound pressure at the time of ignition that there is no harmful effect on passengers.

When a car running at a speed of 50 kilometers per hour collides head-on against an obstacle, a passenger in the car leaves his seat and is thrown forward by inertia in about 30 to 40 milliseconds. Accordingly, the gas-generating composition for inflating the above-mentioned bag must be capable of inflating the bag, which has generally a

volume less than 300 l, with gas within about 300 milliseconds.

The limit of sound pressure level which does not harm passengers at the time of inflation of the above-mentioned bag is about 160 decibels.

The combustible constituents which are used in the present invention and bring about rapid combustion, i.e. oxidation and reduction reactions, comprise a mixture of at least one reducing agent, preferably selected from zirconium, magnesium, boron, aluminium, silicon, and silicon-iron and at least one oxidizing agent, preferably selected from potassium perchlorate, potassium chlorate, potassium bromate, potassium nitrate, ammonium perchlorate, barium nitrate, barium peroxide, lead tetroxide, lead peroxide, lead monoxide, and lead chromate. The mixture may contain secondary materials such as a binding agent.

When the resultant composition is ignited, it initiates a rapid combustion reaction which generates sufficient gas for rapid inflation of the bag.

"Smokeless powder" is a term used in the exposives art to mean a powdered pyroxylin or nitrocellulose explosive which has been processed to produce no smoke on ignition.

When the amount of combustible constituent exceeds 80% by weight, the amount of gas generated becomes insufficient and when the amount of smokeless powder or nitrocellulose exceeds 90% by weight, the combustion speed is reduced. Accordingly, if the above proportions are not observed the practical value of the composition is drastically reduced.

High molecular weight organic polymeric materials useful as gas-generating agents in the present composition include one or more thermoplastic resins, such as polyvinyl chloride, polyethylene, polystyrene, polyethers, polyvinyl-acetate; thermoplastic elastomers, such as styrene-butadiene block copolymers; thermosetting resins, such as polyacetals, epoxy resins; and thermosetting rubbers, such as polyurethanes, polysulfides, polybutadiene, polybutadiene-acrylic acid copolymers. Easily heat-decomposable organic substances include one or more compounds selected from the group consisting of azodicarbonamide, azobisisobutyronitrile, aminoguanidine, hexamethylene tetramine, dicyandiamide and thiourea. They are mostly nitrogen compounds. The use of the above materials provides adequate generation of gas during combustion. The materials can be used alone or in the form of mixtures.

Those compositions comprising 20 to 50% by weight of the combustible constituent and 50 to 80% by weight of the high molecular weight organic polymeric material or easily heat-decomposable organic compound are preferable. If the amount of the combustible constituent exceeds 80% by weight, insufficient gas is generated and if the amount of the high molecular weight organic polymeric material or easily heat-decomposable organic compound exceeds 90% by weight, combustion speed is reduced.

The speed and amount of gas-generation from the gas-generating constituent used in the present invention can be varied optionally in the high speed range by changing the mixing ratio of the oxidizing agent, the reducing agent and the gas-generating agent. In the preparation, these three constituents are usually admixed at the same time. However, it is also possible to prepare in advance, two kinds of different mixtures consisting of a combustible constituent (a mixture of an oxidizing agent and a reducing agent) and a gas generating agent (smokeless powder, nitrocellulose, high molecular weight organic polymeric material or easily heat-decomposable organic substance) or a combustible constituent (a mixture of an oxidizing agent and a reducing agent) and a mixture of a gas generating agent (smokeless powder, nitrocellulose, high molecular weight organic polymeric material or easily heat-decomposable organic substance) and an oxidizing agent, and mix the two kinds optionally at the time of need. In this case it is convenient for mixing and handling if, in advance, the above-mentioned mixtures are made into granules with a suitable binding agent. Further a combustible agent or a combustion-promoting agent can be mixed with the above-mentioned mixtures at the time of need.

The gas-generating composition is obtained, as above-mentioned, by mixing the gas-generating agent with a constituent which causes a combustion reaction which does not produce gas in substantial quantities. With the combination of a high temperature gas accompanying the rapid combustion reaction of a reducing agent and an oxidizing agent, and in addition, a gas produced by the smokeless powder, nitrocellulose, a high molecular weight organic polymeric material or an easily heat-decomposable organic substance, a body protecting bag can be inflated rapidly.

Thus, the gas-producing composition is charged to a vessel, and is installed in a bag. Alternatively, it is made into an arbitrary shape to form cartridges or shaped explosives to which an electric igniting apparatus is attached and is installed in a body protecting bag. When it is then ignited, the rapid expansion of the reaction product gasified by a high heat of formation accompanying a rapid exothermic reaction and the gas produced by the combustion of the gas generating agent inflates the bag instantaneously. By the contraction of gas due to the

subsequent lowering of the temperature, the bag gradually contracts. When an occupant collides against this bag, the repelling force of the bag exerted upon the occupant is thereby reduced and the shock exerted upon the occupant is further diminished. Thus it is an advantage of the use of the present gas-generating composition that the shock absorbing and low repelling characteristics are superior. Since the gas-generating composition is produced by mixing a reducing agent and an oxidizing agent with smokeless powder, nitrocellulose, a high molecular organic polymeric material, or an easily heat-decomposable organic substance, it does not produce a roaring explosion sound and the sound pressure level at the time of ignition is so low that it does not harm occupants.

As above-mentioned, since the gasification reaction proceeds rapidly without roaring explosion sound in the gas generating composition, it is possible to inflate the bag rapidly with such a low level of sound pressure as being not harmful to the auditory function of passengers.

Since the gas-producing composition does not require a high-pressure container, as in case of liquefied gas or compressed gas, the diminished performance because of leakage of gas during storage can be prevented. Also, because the composition can be encapsulated and placed at several places in a folded bag, there is no need to be concerned about installation space required for the gas-generating apparatus and thus mounting onto a car is very easy.

Further, since the reaction product gas of the composition is a high temperature gas, the gas pressure in the bag is not influenced by environmental temperature. Accordingly, the shock-absorbing characteristics of the bag remain at a constant value without being affected by the outside temperature.

The invention is further illustrated by the following examples. All parts and percentages are by weight.

EXAMPLE 1

The following composition was used in this example:

Zirconium	20 parts
Lead tetroxide (Plumbo plumbic oxide) (Pb_3O_4)	79 parts
Chlorinated rubber	1 part

In making this composition, a chlorinated rubber was dissolved in toluene in advance to prepare a binder. The resultant binder was then added to the zirconium and lead tetroxide. They were blended and then granulated.

A gas-generated composition obtained by mixing 4 g of the above-mentioned granular agent with 11 g of smokeless powder, was charged to a polyvinyl chloride pipe. After an ignition device was connected, the filled polyvinyl chloride pipe was installed in a rubber bag having an interior volume of 70 l.

By igniting the gas-generating composition by the input of an electric current to the electric ignition device, the rubber bag expanded up to a sufficiently large volume in 20 milliseconds. The sound pressure level at the time of ignition was 125 decibels.

EXAMPLE 2

The following composition was used in this example:

Zirconium	30 parts
Lead tetroxide (Pb_3O_4)	69 parts
Styrene-butadiene block-copolymer ... (Made by Asahi Kasei Kogyo Co., Ltd., Trade mark: Toughprene)	1 part

The styrene-butadiene block-copolymer was first dissolved in toluene to prepare a binder. The resultant binder was then added to the zirconium and lead tetroxide. The blend was kneaded and granulated.

A gas-generating composition obtained by mixing 5 g of the granular material with 10 g of nitrocellulose, was charged to a polyvinyl chloride pipe. After an ignition device was connected, the filled polyvinyl chloride pipe was installed in a rubber bag having an inner volume of 70 l.

The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the rubber bag expanded up to a sufficiently large

volume in 30 milliseconds. The sound pressure level at the time of ignition was 113 decibels.

EXAMPLE 3

The following composition was used in this example:

Boron	20 parts
Barium peroxide ...	79 parts
Chlorinated rubber	1 part

A granular material was prepared in the same manner as in Example 1, using this composition.

Three 5 g charges of a gas-generating composition obtained by mixing 7 g of the above-mentioned granular material with 8 g of smokeless powder, were respectively put into three polyethylene containers.

The containers were connected to electric ignition devices, sealed, and then installed in a bag of nylon cloth having an inner volume of 70 l, the surface of the nylon cloth being coated with rubber.

The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the bag expanded up to a sufficiently large volume in 29 milliseconds. The sound pressure at the time of ignition was 120 decibels.

EXAMPLE 4

The following composition was used in this example:

Boron	10 parts
Silicon	5 parts
Lead tetroxide	84 parts
Styrene-butadiene block-copolymer ... (Made by Asahi Kasei Kogyo Co., Ltd., Trade mark: Toughprene)	1 part

A granular material was prepared in the same manner as in Example 1, using this composition.

A gas-generating composition obtained by mixing 8 g of the above-mentioned granular material with 8 g of smokeless powder, was charged to a polyvinyl chloride pipe. The filled pipe was connected to an electric ignition device and installed in a bag of nylon cloth having an inner volume of 70 l, the surface of the nylon cloth being coated with rubber.

The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the bag expanded up to a sufficiently large volume in 28 milliseconds. The sound pressure level at the time of ignition was 120 decibels.

EXAMPLE 5

The following composition was used in this example:

Zirconium	20 parts
Lead tetroxide ...	79 parts
Chlorinated rubber	1 part

A granular material was prepared in the same manner as in Example 1 by using this composition.

A gas-generating composition obtained by mixing 10.5 g of the above-mentioned granular material with 4.5 g of nitrocellulose, was charged to a polyvinyl chloride pipe. The pipe was connected to an electric ignition device, and installed in a bag of nylon cloth having an inner volume of 70 l, the surface of the nylon cloth being coated with rubber. The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the bag expanded up to a sufficiently large volume in 18 milliseconds. The sound pressure level at the time of ignition was 118 decibels.

EXAMPLE 6

The following two components were used in this example:

Component A	Boron	5 parts
	Lead tetroxide	95 parts
	Styrene-butadiene block-copolymer ... (Made by Asahi Kasei Kogyo Co., Ltd., Trade mark: Toughprene)	0.5 part
Component B	Ammonium perchlorate	90 parts
	Polybutadiene	10 parts
	Methylaziridinyl phosphine oxide	0.35 part
	Epoxy resin	0.5 part
	Polyvinyl chloride powder	30 parts

Components A and B were separately blended and made into granular materials. Subsequently, the two granular materials were completely mixed in weight ratio of 1:2 (A:B) to prepare a gas-generating composition. 80 g of this gas-generating composition was charged to a polyethylene vessel. The vessel was connected to an electrical ignition device and installed in a bag of nylon having an inner volume of 250 l. The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the time of expansion and unfolding of the bag and the sound pressure level at the time of ignition were measured. The bag expanded and unfolded in 23 milliseconds, and the sound pressure level was 138 decibels.

EXAMPLE 7

The following composition was used in this example:

Barium peroxide	90 parts
Zirconium	10 parts
Azodicarbonamide	200 parts
Styrene-butadiene block-copolymer ... (Made by Asahi Kasei Kogyo Co., Ltd., Trade mark: Toughprene)	1 part

The above composition was thoroughly blended and then granulated.

80 g of this granular material was charged to a polyethylene vessel. The filled vessel was connected to an electric ignition device and installed in a bag of nylon having an inner volume of 250 l. The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the time of expansion and unfolding of the bag and the sound pressure level were measured. As a result, the time was 25 milliseconds and the sound pressure was 140 decibels.

EXAMPLE 8

The following two components were used in this example:

Component A	Lead tetroxide	180 parts
	Boron	5 parts
	Styrene-butadiene block-copolymer ... (Made by Asahi Kasei Kogyo Co., Ltd., Trade mark: Toughprene)	0.5 part
Component B	Polybutadiene	14 parts
	Methylaziridinyl phosphine oxide	0.5 part
	Epoxy resin	1.5 parts

The above-mentioned component A was blended and made into a granular material. Subsequently the component B was mixed, cured and cut into small granules. The two granular agents were completely mixed in a weight ratio of 2:1 (B:A) to prepare a gas-generating composition. 80 g of this gas-generating composition was charged to a polyethylene vessel.

An electrical ignition device was connected to the vessel, which was then installed in a nylon bag having an inner volume of 250 l. The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the time of expansion and unfolding of the confinement and the sound pressure level were measured. As a result, the time was 22 milliseconds and the sound pressure level was 135 decibels.

EXAMPLE 9

Boron (B)	5 parts
Lead tetroxide (Pb_3O_4)	95 parts
Styrene-butadiene block-copolymer ... (Made by Asahi Kasei Kogyo Co., Ltd., Trade mark: Toughprene)	1 part

Styrene-butadiene block-copolymer was dissolved in toluene in advance to prepare a binder. The resultant binder was added to boron and lead tetroxide, and after blending, they were granulated into a granular agent.

A smokeless powder was fully mixed with the above-mentioned granular material in a ratio by weight of the former to the latter of 2:1 to give a gas-generating composition. 80 g of the resultant gas-generating composition was filled in a vessel of polyethylene. The resultant vessel to which an electric ignition device was attached, was installed in a confinement of nylon cloth having a volume of 250 l. The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the time of expansion and unfolding of the bag and the sound pressure level at the time of ignition were measured. As a result, the former was 21 milliseconds, and the latter was 138 db.

EXAMPLE 10

Zirconium (Zr)	21 parts
Lead tetroxide (Pb_3O_4)	79 parts
Styrene-butadiene block-copolymer ... (Made by Asahi Kasei Kogyo Co., Ltd., Trade mark: Toughprene)	1 part

Styrene-butadiene block-copolymer was dissolved in toluene in advance to prepare a binder. The resultant binder was added to zirconium and lead tetroxide, and after blending, they were granulated into a granular material.

A smokeless powder was fully mixed with the above-mentioned granular. material in a ratio by weight of the former to the latter of 2:1 to give a gas-generating composition. 80 g of the resultant gas-generating composition was filled in a vessel of polyethylene. The resultant vessel to which an electric ignition device was attached, was installed in a bag of nylon cloth having a volume of 250 l. The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the time of expansion and unfolding of the bag and the sound pressure level at the time of ignition were measured. As a result, the former was 25 milliseconds, and the latter was 134 db.

EXAMPLE 11

The following two components were used in this example.

Component A	Boron (B)	5 parts
	Lead tetroxide (Pb_3O_4)	95 parts
	Styrene-butadiene block-copolymer ... (Made by Asahi Kasei Kogyo Co., Ltd., Trade mark: Toughprene)	1 part
Component B	Polybutadiene	15 parts
	Methylaziridinyl phosphine oxide	0.5 part
	Epoxy resin	1.5 parts
	Copper chromate ($CuO{\cdot}CrO_3$)	5 parts
	Aluminum (Al)	10 parts
	Ammonium perchlorate	83 parts

The above-mentioned component A was blended in the same manner as in Example 9 to granulate it into a granular material. The above-mentioned component B was then blended, hardened and cut into small granules. The resultant small granules were fully mixed with the above-mentioned granular material in a ratio by weight of component A to component B of 1:3 to give a gas-generating composition. 70 g of the resultant gas-generating composition was filled in a vessel of polyethylene. The filled vessel to which an electric ignition device was attached, was installed in a bag of nylon cloth having a volume of 250 l. The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the time of expansion of the confinement and the sound pressure level at the time of ignition were measured. As a result, the former was 23 milliseconds, and the latter was 140 db.

EXAMPLE 12

Component A	Zirconium (Zr)	21	parts
	Lead tetroxide (Pb_3O_4)	79	parts
	Styrene-butadiene block-copolymer ... (Made by Asahi Kasei Kogyo Co., Ltd., Trade mark: Toughprene)	1	part
Component B	Polybutadiene	15	parts
	Methylaziridinyl phosphine oxide	0.5	part
	Epoxy resin	1.5	parts
	Copper chromate ($CuO{\cdot}CrO_3$)	5	parts
	Aluminum (Al)	10	parts
	Ammonium perchlorate	83	parts

The above-mentioned component A was blended in the same manner as in Example 10 to granulate it into a granular material The component B was then blended, hardened and cut into small granules. The resultant small granules were fully mixed with the above-mentioned granular agent in a ratio by weight of component A to component B of 1:3 to give a gas-generating composition. 70 g of the resultant gas-generating composition was filled in a vessel of polyethylene. The filled vessel to which an electric ignition device was attached, was installed in a bag of nylon cloth having a volume of 250 l. The gas-generating composition was then ignited by the input of an electric current to the electric ignition device, and the time of expansion of the bag and the sound pressure level at the time of ignition were measured. As a result, the former was 28 milliseconds, and the latter was 135 db.

WHAT WE CLAIM IS:—

1. A vehicle safety device comprising an inflatable bag, a gas generating composition positioned within the bag or in a space communicating with the bag, and means for initiating gas generation, the gas-generating composition comprising:
   (A) 10% to 80% by weight of a combustible constituent comprising:
      (1) at least one reducing agent, and
      (2) at least one inorganic oxidizing agent; and
   (B) 20% to 90% by weight of a gas-generating agent comprising one or more of smokeless powder, nitrocellulose, combustible high molecular weight organic polymeric material and organic compounds easily decomposable by heat.

2. A device according to claim 1, wherein the reducing agent is zirconium, magnesium, boron, aluminium, silicon or silicon-iron, and the inorganic oxidizing agent is potassium perchlorate, potassium chlorate, potassium bromate, potassium nitrate, ammonium perchlorate, barium nitrate, barium peroxide, lead tetroxide, lead peroxide, lead monoxide, or lead chromate.

3. A device according to claim 1 or claim 2, wherein the combustible high-molecular weight organic polymeric material is polyvinyl chloride, polyethylene, polystyrene, a polyacetal, polyvinyl acetate, a styrene-butadiene copolymer; a polyether, an epoxy resin, a polyurethane, a polysulfide, a polybutadiene or a polybutadiene-acrylic acid copolymer.

4. A device according to any one of the preceding claims wherein the easily-heat-decomposable organic compound is azodicarbonamide, azobisisobutyronitrile, aminoguanidene, hexamethylene tetramine, dicyandiamide or thiourea.

5. A vehicle safety device substantially as described in any one of the Examples.

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